ELSEVIER

Spectrochimica Acta Part A 51 (1995) 1725–1737

SPECTROCHIMICA ACTA PART A

Temperature and solvent effects on the infrared *e*-type bands of methyl iodide: orientational diffusion and free rotation

A.A. Stolov [a,*], A.I. Morozov [a], A.B. Remizov [b]

[a] *Kazan State University, Lenin st., 18, Kazan 420008, Russia*
[b] *Kazan State Technological University, Karl Marx st., 68, Kazan 420015, Russia*

Received 12 May 1994; in final form 23 November 1994; accepted 25 November 1994

Abstract

Infrared absorption spectra of liquid methyl iodide (CH_3I) and its solutions in CCl_4, CS_2, heptane, benzene, chloroform and deuterated acetone-d_6 have been studied. Infrared spectra in the regions 3400–2700, 1700–1100 and 1000–750 cm^{-1} were fitted by the sum of components, with the form of multiplication of the Lorentzian and Gaussian functions. *E*-Type bands under investigation ($\nu_4 = 3047$, $\nu_5 = 1428$, and $\nu_6 = 885\ cm^{-1}$) were reproduced by the sums of two components: the narrower (n) and the broader (b) ones. A different temperature behaviour of the components has been found: the integrated intensity of the narrower component (I_n) decreases with the temperature, while the intensity of the broader one (I_b) increases. The narrower components of ν_5 and ν_6 were attributed to CH_3I molecules moving according to the orientational diffusion mechanism; the broader ones were attributed to molecules, freely rotating about the C_{3v} axis. Some additional mechanism (probably the interactions between CH stretching vibrations with single particle and collective motions of molecular dipoles) was proposed to play a part in forming the ν_4 bandshape. The enthalpy difference between freely rotating molecules and those moving via an orientational diffusion mechanism (ΔH) have been determined by the slopes of the dependencies of $\ln(I_n/I_b)$ upon T^{-1}: $\Delta H = 0.8 \pm 0.1$ kcal mol^{-1}. The temperature behaviour of δ_n has been studied in the 210–340 K temperature range, and Rakov's approach has been used to determine the activation enthalpy (ΔH^*) and entropy (ΔS^*) of parallel orientational diffusion in the pure liquid: $\Delta S^* = -4.5 \pm 0.2$ cal $mol^{-1}\ K^{-1}$, $\Delta H^* = 0.1 \pm 0.1$ kcal mol^{-1}. The CH_3 stretching range was found to be strongly affected by a solvent. Total integral absorption coefficients of ν_1 and ν_4 bands increase two-fold when going from CCl_4 to acetone-d_6 solution, while δ_n values decrease by 3–9 cm^{-1}. The observed effects were explained in terms of the existence of complexes with weak $ICH_3 \cdots$ acetone hydrogen bonding. The strength of the hydrogen bonding was characterized by enthalpies of specific interaction $\Delta H_{int.}^{CH_3I/S}$ (sp.). These values were estimated by the "intensity rule": $\Delta H_{int.}^{CH_3I/S}$ (sp.) = 0.13 kcal mol^{-1} for self-association in pure CH_3I and 0.4 kcal mol^{-1} for solution in acetone-d_6.

1. Introduction

Methyl iodide (CH_3I) and its deuterated derivatives are the simplest symmetric top molecules having essentially different moments of inertia for parallel and perpendicular rotation. It is not surprising that these compounds were used as models when analyzing the general principles of vibrational and orientational relaxation in molecules [1–7]. Infrered and Raman spectra of CH_3I were extensively studied during a period of several decades [1–20] and the agreement of the data obtained for a_1-type bands seems to be

* Corresponding author.

SSDI 0584-8539(95)01338-5